REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
23-03-2012	final report	March, 1st, 2009 - March, 1st, 2012

4. TITLE AND SUBTITLE
High Power Electrochemical Capacitors

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA9550-09-1-0176

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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8. PERFORMING ORGANIZATION REPORT NUMBER
3

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Sponsoring Agency: AFOSR
Program Manager: Dr. John Luginsland
Directorate: Physics and Electronics
Research Area: Electro-Energetic Physics

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-OSR-VA-TR-2012-0997

12. DISTRIBUTION/AVAILABILITY STATEMENT
Distribution A: Approved for Public Release

13. SUPPLEMENTARY NOTES
N/A

14. ABSTRACT
Electrochemical supercapacitors are rechargeable electrochemical energy storage devices similar to batteries, but with different performance characteristics. Supercapacitors can store more power in a smaller volume and often at a lower cost. In contrast to batteries, supercapacitors have incredibly long cycle life (> 1000,000 cycles), and could be charged in less than a second. Their unique characteristics allow them to complement batteries in applications where high power and low weight are essential, including directed-energy weapons, compact pulsed power, mobile power quality devices, and peak power sources for aircraft and electric vehicles. In our project we focus on materials for high energy / high power supercapacitors.

15. SUBJECT TERMS
supercapacitors, composite, carbon

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Gleb Yushin
A	A	A	N/A		19b. TELEPHONE NUMBER *(Include area code)* 267-679-3219

Final report: High Power Electrochemical Capacitors

AFOSR: FA9550-09-1-0176; Start date: March, 1st, 2009

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1. Contributors to this project

Sofiane Boukhalfa (Ph.D. student), *Yair Korenblit* (PhD student), *Adam Kajdos* (undergraduate student), *Wei Lu* (part-time research assistant), *Igor Kovalenko* (part-time research associate), *Kara Evanoff* (part-time research assistant)

2. Publications and presentations during the last year

2.1. International meetings

1. G. Yushin, *Hierarchical Self-Assembled Materials for Energy-Related Applications*, invited to give a **keynote lecture** at a 2012 Spring MRS meeting, San Francisco, USA (2012).
2. G. Yushin, *Nanodiamond for Energy-Related Applications*, invited to give a 2nd **keynote lecture** at a 2012 Spring MRS meeting, San Francisco, USA (2012).
3. G. Yushin, *Nanostructured Materials for Energy Storage Application*s, GORDON Research Conference (GRC) on Electrochemistry taken place in Ventura, CA (2012) **(invited)**
4. G. Yushin, *Nanocomposite Materials for Energy Storage and Multifunctional Application*s at TMS, Orlando, FL (2012) **(invited)**
5. G. Yushin, *Nanocomposite Carbon-Containing Materials for Energy Storage and Multifunctional Application*s, at the Workshop on "Carbon Materials for Energy" organized by Fraunhofer IWS, Dresden, Germany (**a keynote lecture)**.
6. G. Yushin, *Nanocomposite Materials for High Energy Supercapacitors and Li-ion Batteries*, at the 1st NSF-sponsored US-Taiwain Workshop for Materials and Systems "Challenges in Electrical Energy Storage", Taipei, Taiwan (2011) **(invited)**
7. G. Yushin, *Nanostructured Materials for Energy Storage Application*s, at the 10X Advanced Battery R&D Conference, Santa Clara, CA, USA (2011) **(invited)**
8. Y. Korenblit, A. Kajdos, G. Yushin, *Tailoring the Pore Alignment for Rapid Ion Transport in Microporous Carbons*, MRS Spring Meeting, San Francisco, CA (2011).
9. I. Kovalenko and G. Yushin, *Detonation Nanodiamond and Onion-like Carbon - Embedded Polyaniline for Supercapacitors*, MRS Spring Meeting, San Francisco, CA (2011).

10. G. Yushin, *Nanostructured Materials for Energy Storage Application*s, at the 10X Advanced Battery R&D Conference, which took place in Santa Clara, CA, USA (2010) **(invited)**

11. G. Yushin, *Nanocomposite Materials for Energy Storage Applications*, at the 2nd UNIST International Conference, which took place in Ulsan, Korea (2010) **(invited)**

12. B. Hertzberg, S. Boukhalfa, A. Magasinski, I. Kovalenko, P. Dixon, and G. Yushin, *Carbon-Containing Nanocomposite Materials for Energy Storage*, American Chemical Society, Boston, MA (2010) **(invited)**.

13. S. Boukhalfa, A. Magasinski, B. Hertzberg, L. Wei, G. Yushin, *Metal-Oxide / Carbon Nanocomposites for Use in Supercapacitors*, 2010 World Conference on Carbon, Clemson, SC (2010)

14. A. Kajdos, A. Kvit, J. Jagiello, G. Yushin, *Ion Diffusion in Electrical Double Layer Capacitors Based on Microporous Carbons*, ECS meeting, Vancouver, Canada (2010)

15. A. Magasinski, B. Hertzberg, Y. Korenblit, I. Kovalenko, A. Kajdos, G. Yushin, *Novel Materials for Advanced Supercapacitors and Li-ion Batterie*s, The 76th Annual Meeting of the Southeastern Section of the American Physical Society, Atlanta, GA (2009).

a. Student Awards

1) NSF GSPC Award and a travel grant to participate in a 3rd International Conference from Nanoparticles and Nanomaterials to Nanodevices and Nanosystems (IC4N) and the Cretan Workshop on: Global Challenges and Opportunities for Nanotechnology, Crete, Greece (Sofiane Boukhalfa) , 2011

2) Best Poster Award at the ASM International Atlanta's Chapter Student Poster Competition (Yair Korenblit), 2010

3) The "runner-up" (2nd place) Poster Award in the in the undergraduate student at the ASM International Atlanta's Chapter Student Poster Competition (Adam Kajdos), 2010

4) Phi Kappa Phi Award (the Single Most Prestigious Academic Award made annually to the most outstanding undergraduate student at Georgia Tech) – (Adam Kajdos), 2010

5) College of Engineering Outstanding Undergraduate Researcher Award (the best undergraduate researcher in the College) (Adam Kajdos), 2010

6) Henry Ford II Scholar Award (Adam Kajdos)

7) Presidential Undergraduate Research Award (Adam Kajdos, Frank Jones), 2009

8) 1st Place Oral Presentation Award at the Annual Georgia Tech Graduate Research Symposium (Yair Korenblit), 2009

9) 1st Place Oral Presentation Award at the Annual Georgia Tech Graduate Technical Symposium (Yair Korenblit), 2009

10) 1st Place Poster Presentation Award at the Annual Georgia Tech Graduate Technical Symposium (Yair Korenblit)

b. Papers published

1. S. Boukhalfa, K. Evanoff and G. Yushin, *Atomic Layer Deposition of Vanadium Oxide on Carbon Nanotubes for High-Power Supercapacitor Electrodes*, **Energy & Environmental Science (IF=9.5)** DOI:10.1039/C2EE21110F, 2012
2. J. Benson, S. Boukhalfa, A. Magasinski, A. Kvit and G. Yushin, *Chemical Vapor Deposition of Aluminum Nanowires on Metal Substrates for Electrical Energy Storage Applications,* **ACS Nano (IF=10),** 2012
3. Y. Korenblit, A. Kajdos, W.C. West, M.C. Smart, E.J. Brandon, A. Kvit, J. Jagiello and G. Yushin, *In-Situ Studies of Ion Transport in Microporous Supercapacitor Electrodes at Ultra-Low Temperatures***, Advanced Functional Materials (IF=8.5),** 2011
4. L. Wei, M. Sevilla, A. B. Fuertes, R. Mokaya and G. Yushin, *Polypyrrole-Derived Activated Carbons for High-Performance Electrical Double-layer Capacitors with Ionic Liquid Electrolyte,* **Advanced Functional Materials (IF=8.5),** 2011
5. L. Wei, M. Sevilla, A.B. Fuertesc, R. Mokaya, G. Yushin, *Hydrothermal Carbonisation of Abundant Renewable Natural Organic Chemicals for High-Performance Supercapacitor Electrodes*, **Advanced Energy Materials**, 2011, 1, p.356–361.
6. M. Rose, Y. Korenblit, E. Kockrick, L. Borchardt, M. Oschatz, S. Kaskel and G. Yushin, *Hierarchical Micro- and Mesoporous Carbide-Derived Carbon as a High-Performance Electrode Material in Supercapacitors*, **Small (IF=7.3)**, 2011, 7 (8), p. 1108-1117.
7. I. Kovalenko, D. Bucknall, G. Yushin, *Detonation Nanodiamond and Onion-like Carbon - Embedded Polyaniline for Supercapacitors*, **Advanced Functional Materials (IF=8.5)**, 2011, 20 (22), p. 3979-3986
8. Y. Korenblit, M. Rose, E. Kockrick, L. Borchardt, A. Kvit, S. Kaskel, G. Yushin, *High-Rate Electrochemical Capacitors Based on Ordered Mesoporous Silicon Carbide-Derived Carbon***, ACS Nano (IF=10),** 2010, 4 (3), p. 1337-1344.
9. A. Kajdos, F. Jones, A. Kvit, J. Jagiello, G. Yushin, *Tailoring the Pore Alignment for Rapid Ion Transport in Microporous Carbon,* **JACS Communications (IF=9)**, Article ASAP, 2010, 132 (1) p. 3252.
10. M. Oschatz, E. Kockrick, M. Rose, L. Borchardt, N. Klein, I. Senkovska, T. Freudenberg, Y. Korenblit, G. Yushin, S. Kaskel, *A Cubic Ordered Mesoporous Carbide Derived Carbon for Gas and Energy Storage Applications***, Carbon (IF=4.5),** 2010, 48(14), p. 3987-3992
11. J. Huang, B. Sumpter, V. Meunier, G. Yushin, C. Portet, Y. Gogotsi, *Curvature effects in carbon nanomaterials: Exohedral versus endohedral supercapacitors,* **Journal of Materials Research (IF=2),** 2010, 25(8), p. 1525-1531

3. Collaborators

1. Group of *Prof. Stefan Kaskel*, Direktor, Institut für Anorganische Chemie, Technische Universität Dresden, German

2. Group of *Prof. Robert Mokaya*, School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD (U. K.)

4. Introduction

Electrochemical supercapacitors are rechargeable electrochemical energy storage devices similar to batteries, but with different performance characteristics[1] (Fig. 1). Supercapacitors can store more power in a smaller volume and often at a lower cost. In contrast to batteries, supercapacitors have incredibly long cycle life (> 1000,000 cycles), and could be charged in less than a second. Their unique characteristics allow them to complement batteries in applications where high power and low weight are essential, including directed-energy weapons, compact pulsed power, mobile power quality devices, and peak power sources for aircraft and electric vehicles.

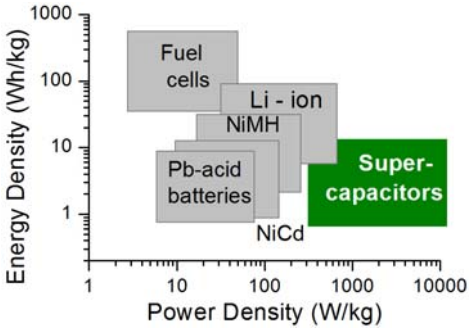

***Fig. 1**. Schematic of power and energy density*

In our project we focus on carbon-based supercapacitors with aligned pores with (and without) uniformly deposited coatings of high capacitance material (e.g. metal oxide coating).

5. Selected Results

ALD-coated Carbon Nanotube Electrodes for Supercapacitors

In this project we use of Atomic Layer Deposition (ALD) to coat highly conductive carbon nanotube (CNT) electrodes with highly capacitive Vanadium Oxide (VO_x) thin film and nanoparticles. The produced electrodes combine the high conductivity and high surface area of CNT with the high specific capacitance of the transition metal oxides. Multi-walled CNTs have been subjected to acid purification step to increase reactivity, introduce defects and surface functionalities, which helps increase the rate of electron transfer and facilitates VO_x deposition onto the CNT surface. This approach bypasses use of a polymeric binder which adds resistance to the device.

ALD allows one to uniformly deposit metal oxides on porous CNT or carbon nanofiber electrodes, thus offering a novel route for the formation of binder-free supercapacitor electrodes with controlled porosity and greatly increased electrical conductivity and specific capacitance. The ability to precisely control the coating thickness and microstructure permits systematic studies of the ion intercalation and diffusion into the bulk of the electrodes. Electrochemical measurements revealed stable performance of the vanadium oxide-coated CNT electrodes with excellent capacitance retention at high current densities or sweep rates. Decreasing the coating thickness to ~10 nm allows one to achieve very high capacitance

of the vanadium oxide with values approaching ~1400 $F \cdot g^{-1}$. Such high capacitance values are unprecedented for supercapacitor electrodes measured in a symmetrical two-electrode configuration in aqueous electrolytes. Our results indicate the importance of the electrode uniformity, precise control over the conformity and thickness of the oxide coatings, and promise of the application of ALD techniques for supercapacitors. Our future efforts will focusing on the application of ALD technique to the deposition of other metal oxides, optimization of oxide layer microstructure, and the use of smaller diameter CNTs are expected to further improve the specific capacitance of the composite electrodes.

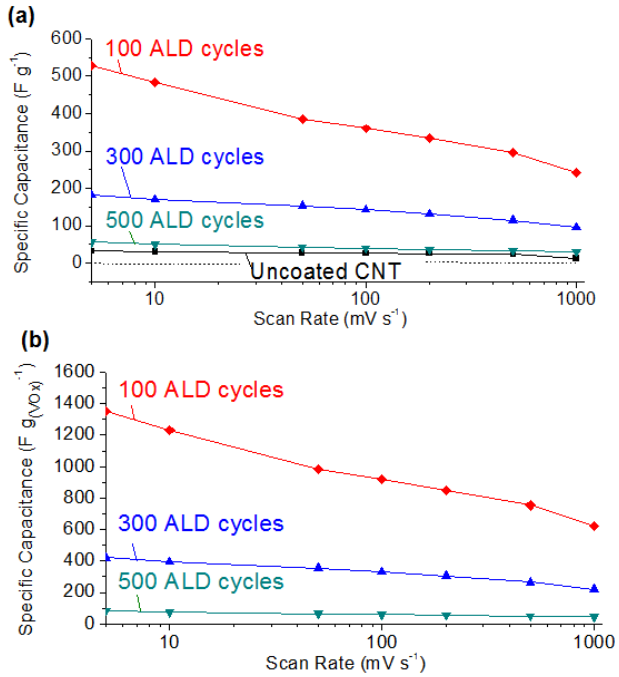

Figure 2. Room temperature specific capacitance of the synthesized CNT-VO_x samples: (a) composite electrode and (b) contribution of VO_x coating. The specific capacitance was calculated from the cyclic voltammetry curves recorded at the sweep rates ranging from 1 to 1000 mV/s in a symmetric two-electrode configuration.

ALD-coated Carbon Al Nanowire Electrodes for Supercapacitors

Potential use of metal nanowires (NWs) is rapidly growing. Currently, conductive carbon nanotubes (CNTs) mass-produced by chemical vapor deposition (CVD) are explored in some of the discussed above applications. However, the CNT structure suffers from the lack of surface sites available for the formation of chemical bonds with the deposited functional layers (such as metal oxide coatings).[2-6] While surface oxidation of multi-walled CNTs allows for the formation of defects and carboxylic surface groups on their outer walls, the concentration of the functional groups on a CNT surface is significantly smaller than what is available on the metal surfaces. As a result, the quality of a CNT/metal oxide interface is generally inferior to that of a metal/metal oxide one.[7] More importantly, due to the low concentration of free electrons in CNT, the dc electrical conductivity of CNT is orders of

magnitude smaller than that of Cu, Al, Au or Ag. Therefore, for most applications requiring high surface area conductors [2-6, 8] with low resistance and high concentration of bonding cites on their surface, NWs of low-cost lightweight highly conductive metals (such as Al) may provide superior performance than CNTs.

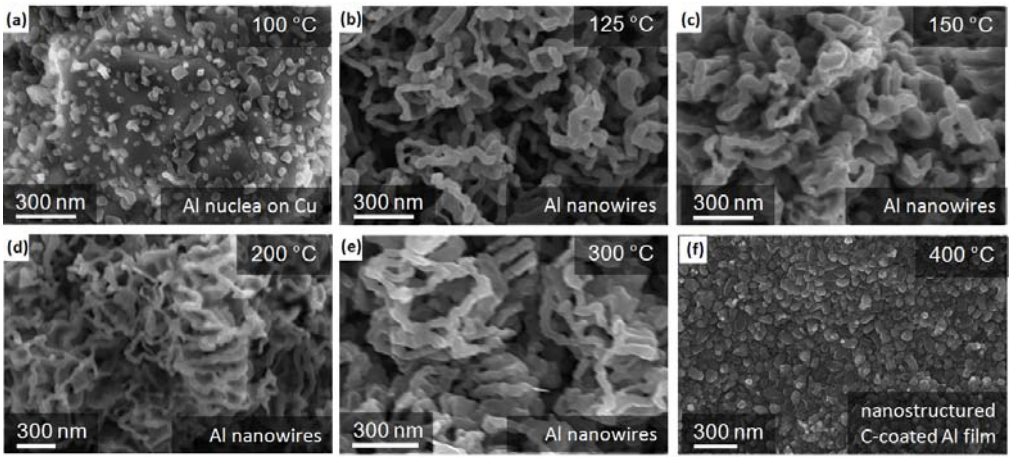

Figure 3. SEM micrographs of CVD deposition of Al NWs onto rough Cu foils at different temperatures: **(a)** 100 °C, **(b)** 125 °C, **(c)** 150 °C, **(d)** 200 °C, **(e)** 300 °C, and **(e)** 400 °C

Another sponsored project allowed us to achieve for the first time a patterned growth of freestanding Al NWs (Fig. 3) on Ni, Fe, and Cu surfaces using trimethylamine alane (TMAA) as an organometallic CVD precursor. For this project we further demonstrated that the ALD deposition of metal oxides on Al NW surface allows one to achieve one of the highest volumetric capacitances reported to date for supercapacitor applications. In our proof-of-concept studies we utilized vanadium oxide (VO_x) as a coating material due its chemical stability, wide availability, and the large potential window for oxidation/reduction reactions to occur.[9-16] Similar to the previously described project, in order to synthesize Al NW – VO_x composite electrodes we employed atomic layer deposition (ALD) to uniformly deposit VO_x onto Al NW substrates. To the best of our knowledge, we are the first group to employ ALD technique for supercapacitor applications. The VO_x coated Al nanowire electrodes with 30-50% of the pore volume available for electrolyte access show volumetric capacitance of 1390-1950 F/cc, which exceeds the volumetric capacitance of porous carbons and many carbon-metal oxide composites by more than an order of magnitude. [17-24]

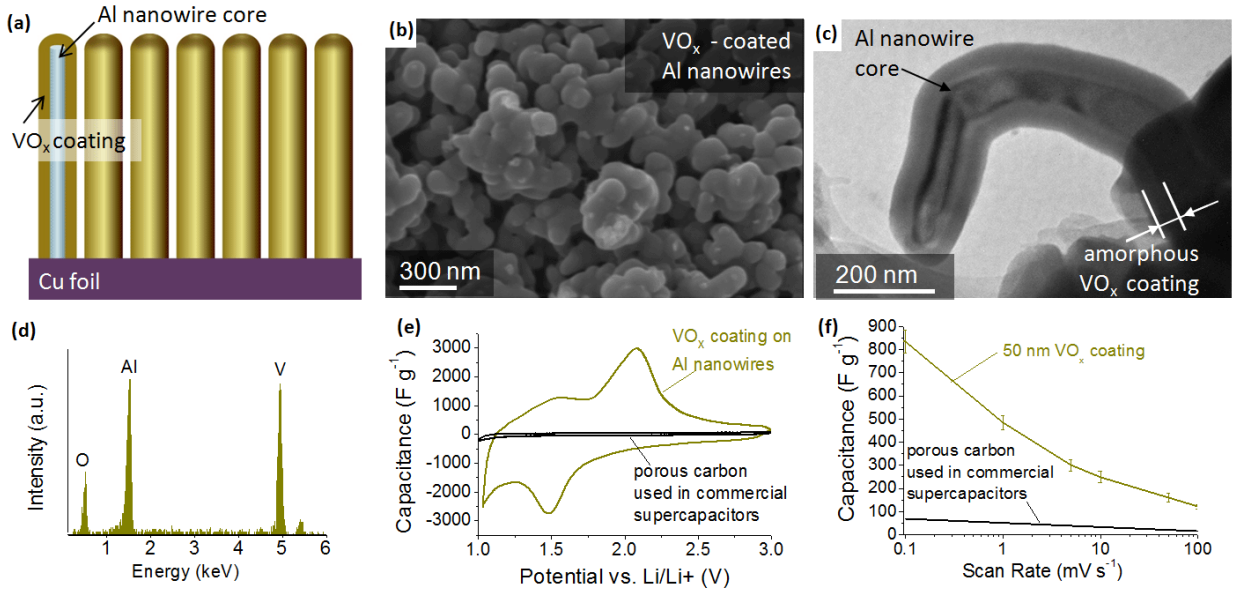

Figure 4. Al nanowire - based supercapacitor: **(a)** simplified schematic of the electrode; **(b)** SEM and **(c)** TEM micrographs of VO_x-coated Al nanowires; **(d)** EDS spectrum of VO_x-coated Al nanowires; **(e)** cyclic voltammetry recorded at 0.1 mV/s for VO_x-coated Al nanowire electrode in comparison to that of porous carbon (capacitance is normalized by the active mass); **(f)** average capacitance as a function of a slew rate for 50 nm VO_x coatings in comparison to that of activated carbon.

Carbide-Derived Carbons with Aligned Pores for Supercapacitors Based on Aqueous Electrolytes and Ionic Liquids.

Ordered mesoporous carbide-derived carbon (OM-CDC) materials produced by nanocasting of ordered mesoporous silica templates are characterized by a bimodal pore size distribution with a high ratio of micropores. The micropores result in outstanding adsorption capacities and the well-defined mesopores facilitate enhanced kinetics in adsorption processes. In out fist year Annual report we described the formation of Carbide Derived Carbons with tightly controlled micropores and aligned mesopores. In our initial studies we performed electrochemical characterization of these carbons in organic electrolytes. In this year we demonstrated a systematic study of the effects of synthesis temperature on the electrochemical performance of these materials in supercapacitors based on a 1 M aqueous solution of sulfuric acid and 1-ethyl-3-methylimidazolium tetrafluoroborate ionic liquid. The cyclic voltammetry showed the specific capacitance of OM-CDC exceeds 200 F/g in the aqueous electrolyte and 185 F/g in the ionic liquid, when measured in a symmetric configuration in the voltage range of up to 0.6 and 2V, respectively (Fig. 5-6). The ordered mesoporous channels in the produced OM-CDC serve as ion-highways and allow for very fast ionic transport into the bulk of the OM-CDC particles. At room temperature the enhanced ion transport led to 75% and 90% of the capacitance

retention at current densities in excess of ~10A/g in ionic liquid and aqueous electrolytes, respectively. The supercapacitors based on 250-300 µm OM-CDC electrodes demonstrated operating frequency of up to 7 Hz in aqueous electrolyte. The combination of high specific capacitance and outstanding rate capabilities of OM-CDC is unmatched by state-of-the art activated carbons and strictly microporous CDC.

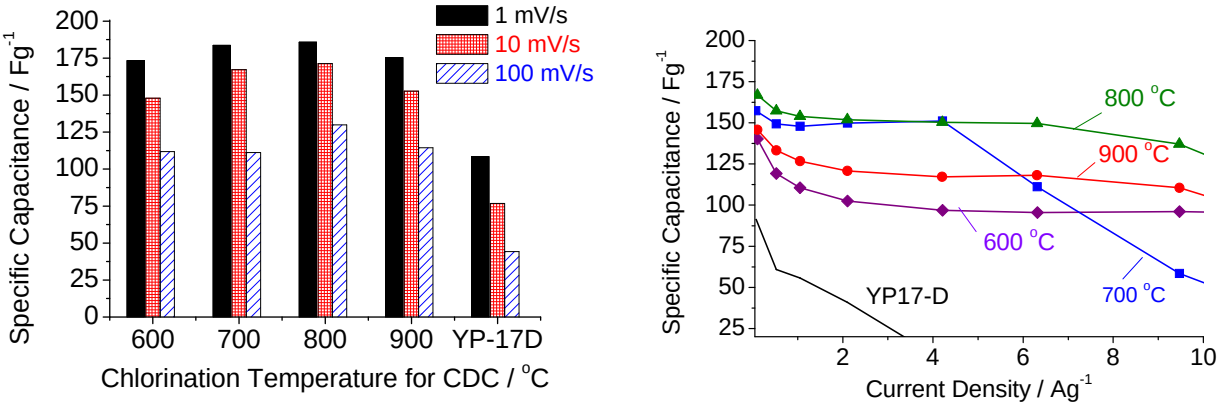

Figure 5. Room temperature performance of OM-CDC-based supercapacitors in 1-ethyl-3-methylimidazolium tetrafluoroborate ionic liquid.

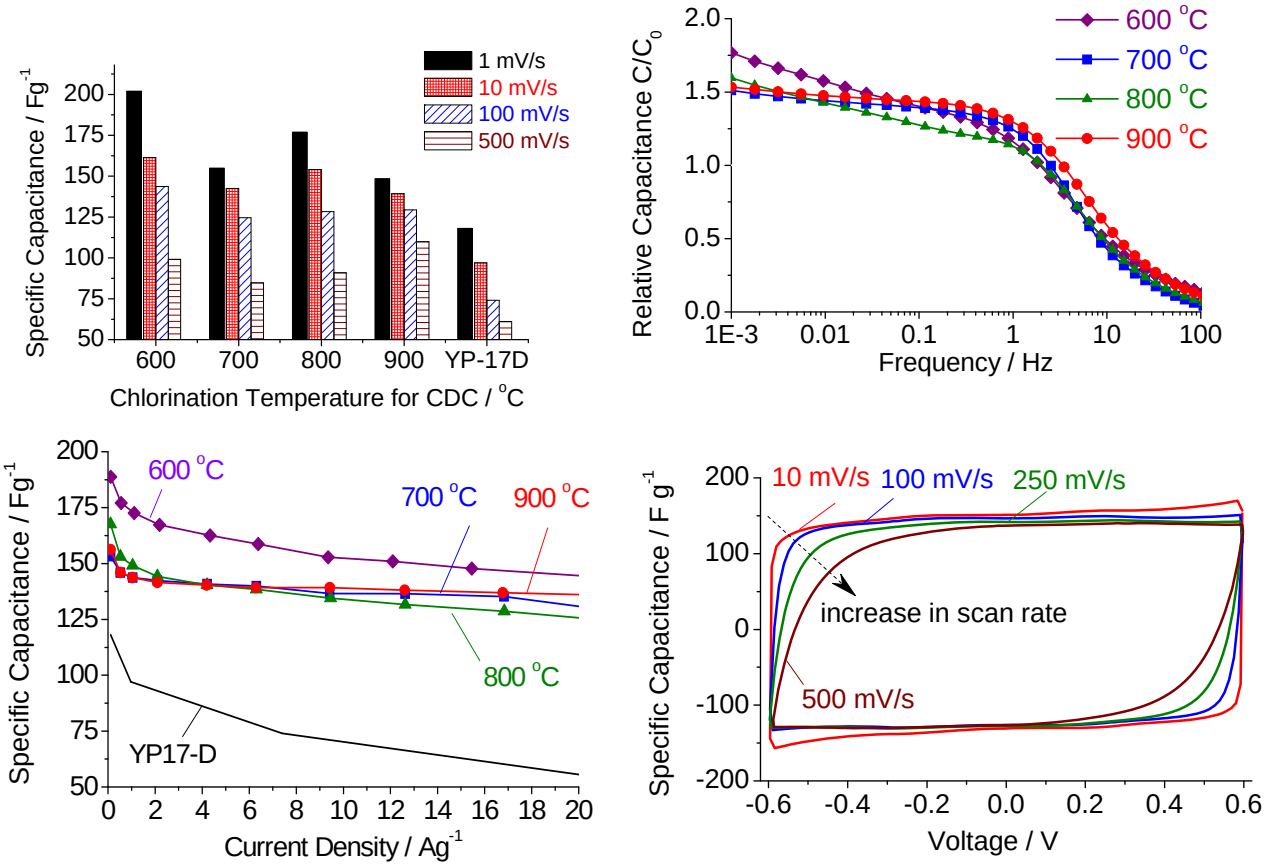

Figure 6. Room temperature performance of OM-CDC-based supercapacitors in aqueous electrolyte.

Supercapacitors for ultra-low temperature operation.

The ability to store and quickly deliver a significant amount of electrical energy at ultra-low temperatures is critically important for energy-efficient operation of high altitude aircraft and spacecraft as well as the exploration of the natural resources available in Polar Regions and mountains. Commercial state of the art high-power rechargeable batteries and electrochemical supercapacitors fail to operate at temperatures below - 40 ºC. Both the severely reduced electrolyte conductivity and dramatically hampered solid state diffusion [25-26] in high-power rechargeable Li-ion batteries currently limit commercial products to a minimum operational temperature of - 20 ºC [25-26]. Some of these limitations can be overcome by using electrochemical double layer capacitors (EDLCs), often described as supercapacitors. These alternative high-power electrochemical energy storage devices do not require solid state diffusion and permit a stable operation with a much wider variety of electrolyte salts and solvents [27-28]. Thus, they are of particular interest for further development and use at ultra-low temperatures [29-30].

In this project we demonstrated that the application of microporous carbon electrodes with aligned pores and 0.5 M solution of spiro-(1,1')-bipyrrolidinium tetrafluoroborate salt in a 1:1 mixture of acetonitrile and methyl formate electrolyte allows fabrication of supercapacitors with an outstanding performance at temperatures as low as - 60 and - 70 ºC (Fig. 7). At such low temperatures the specific capacitance of the synthesized electrodes is up to 123 F/g (71 F/cc), which is nearly 50 % higher than that of the most common commercial supercapacitor electrodes at room temperature. At - 60 ºC selected supercapacitors based on 300 μm electrodes exhibited characteristic charge-discharge time constant of less than 9 s, which is faster than the majority of commercial devices at room temperature. The achieved combination of high supercapacitor energy and power densities at such low temperatures is unprecedented.

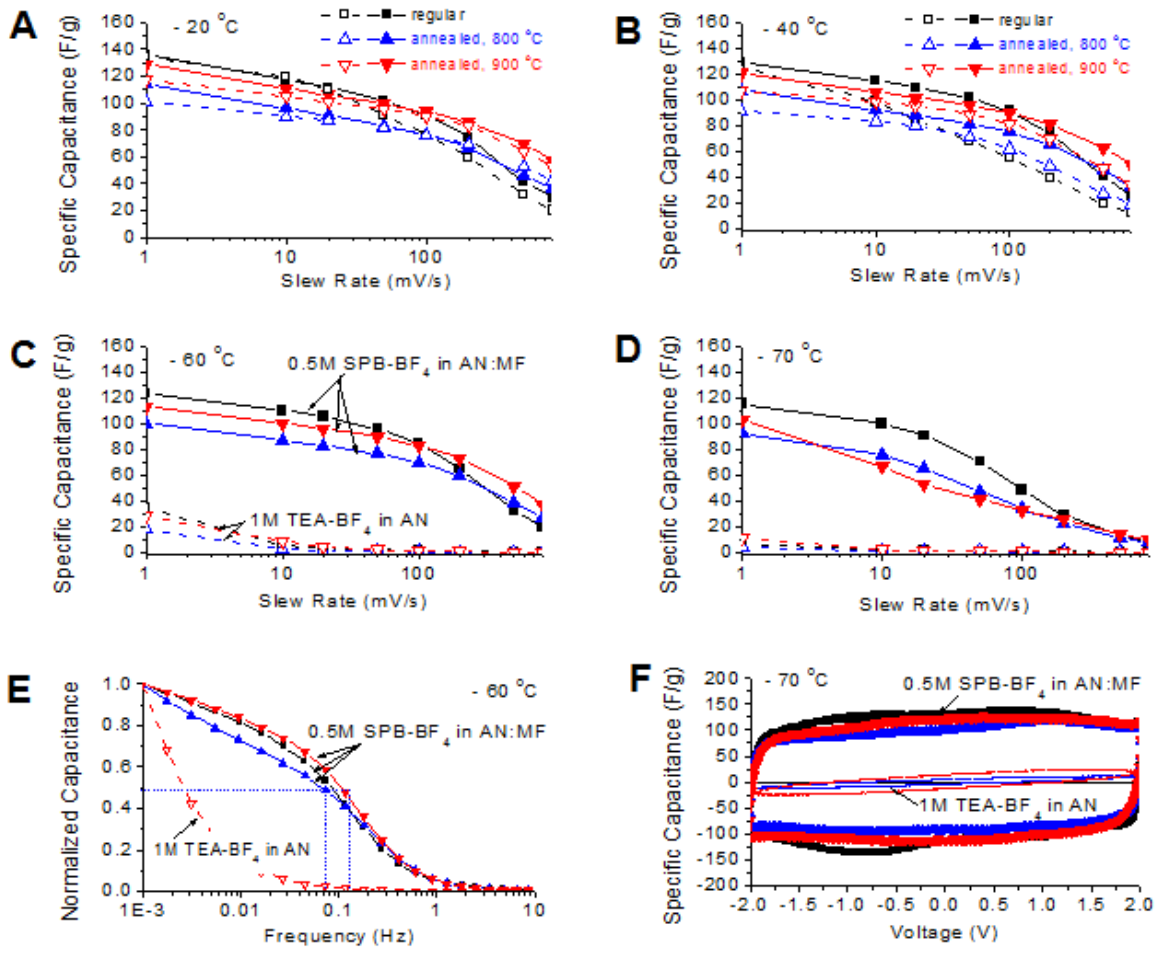

Figure 7. Low temperature performance of supercapacitors in conventional (1M TEA-BF_4 in AN; hollow symbols) and newly developed (0.5 SPB-BF_4 in AN:MF=1:1; solid symbols) electrolytes: specific capacitance calculated from the CV curves as a function of sweep rate at **(A)** -20 ºC, **(B)** -40 ºC, **(C)** – 60 ºC, and **(D)** -70 ºC; **(E)** frequency response of capacitances at -60 ºC and **(F)** cyclic voltammograms at a slew rate of 1 mV/s recorded at – 70 ºC.

Detonation Nanodiamond and Onion-like Carbon - Embedded Polyaniline for Supercapacitors

The detonation nanodiamond is a versatile low-cost nanomaterial with tunable properties and surface chemistry. In this work, we show how the application of nanodiamond (ND) can greatly increase the performance of electrochemically active polymers, such as polyaniline (PANI). Symmetric supercapacitors containing PANI-ND nanocomposite electrodes with 3-28 wt.% ND showed dramatically improved cycle stability and higher capacitance retention at fast sweep rate than pure PANI electrodes. Contrary to other PANI-carbon nanocomposites, specific capacitance of the selected PANI electrodes with embedded ND increased after 10,000 galvanostatic cycles and reached 640 F/g, when measured in a symmetric two-electrode configuration with 1M H_2SO_4 electrolyte. The demonstrated specific

capacitance is 3-4 times higher than that of the activated carbons and more than 15 times higher than that of ND and onion-like carbon (OLC).

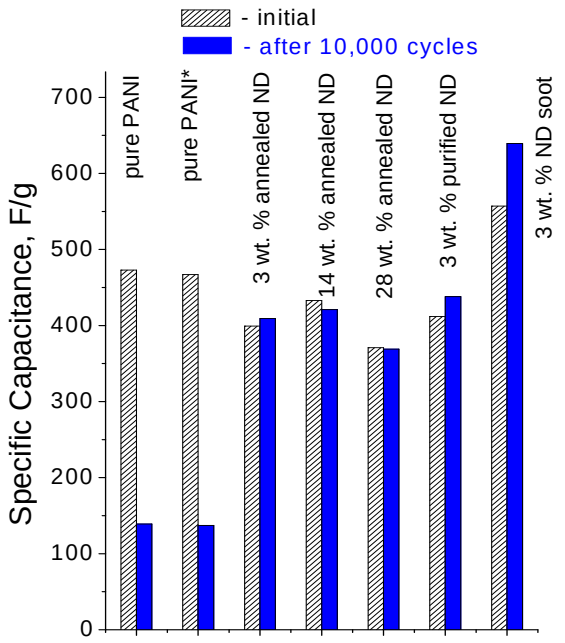

Figure 8. Room temperature specific capacitance of the synthesized composite samples before and after 10,000 cycles. Pure PANI* sample contains 3 wt. % annealed ND mechanically mixed with PANI particles. Other samples contain ND embedded into the PANI particles. The specific capacitance was calculated from the cyclic voltammetry curves recorded at the sweep rate of 1mV/s in a symmetric two-electrode configuration.

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